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(54) BIOCIDALLY ACTIVE GRANULATED COMPOSITION

(71) We, RIEDEL-DE HAEN AKTIENGESELLSCHAFT, a body corporate organised under the laws of Germany, of 3016 Seelze, Germany, do hereby declare the invention, for which we pray that a patent may be granted to us, and the method by which it is to be performed, to be particularly described in and by the following statement:—

The present invention relates to biocidally active granulated compositions.

According to the invention, a process for the production of a biocidally active composition comprises forming an aqueous suspension containing 10—50% by weight of a particulate absorbent carrier having a maximum particle diameter of 5 mm, 0.5 to 40% by weight of a biocidally active ingredient and from 2 to 10% by weight of water soluble polymers, at least two different polymers being present each of which is a polyalcohol, polyester, polyglycol, polyamide or lignin sulfonate, and spray-drying the suspension under mild conditions, as hereinafter defined, to produce granules having an average particle size between 200 and 300 μ.

Granules produced by the method of the invention may have an active ingredient content as high as 70% by weight but are capable, following application in the field, of disintegrating in independent stages to an ultimate average diameter of 0.1 to 5 μ. In general, such aqueous suspensions contain from about 40 to 60% by weight of water. The pressure therein of the two water-soluble polymers not only is responsible for the aforesaid multiple stage disintegration of the product to a smaller particle size, but also provides a suspension which is readily pumpable and susceptible to spray drying techniques.

Biocidally active granulated compositions having average particle diameters of between 0.5 and 1.5 mm are known in the prior art. These products are prepared by grinding and screening, applying the biocidally active compound to a granulated or particulated absorbent carrier or by granulating in special apparatus such as rotary drums, extrusion presses, etc. On application in the field, it is generally necessary to use from about 40 to about 120 kg/hectare. It would obviously be beneficial to be able to reduce the application rate and obtain the same results. For this purpose, efforts have been made to arrive at granulated compositions having an average particle diameter of 0.25 mm down to 0.05 mm. Smaller particle sizes are not feasible since such products tend to be dispersed by wind or air currents and damage adjacent crops. A granulate having an average particle size below 0.25 mm would, in the case of ordinary herbicidal usage having an active ingredient content of between 10 and 60% by weight, require an application rate of only 6 to 10 kg/hectare.

It will further be appreciated that biocidally active granulated compositions having average particle diameters below 0.25 mm must also permit uniform coverage on application and effective diffusion of the active ingredient from the granulate, especially in the case of agents which function through systemic action. In other words, mere attainment of a particle size less than 0.25 mm does

not necessarily assure a more satisfactory product.

The product of the instant invention has the desired fine average particle size (from 200 to 300μ), permits uniform coverage or distribution without dispersal by wind or air currents and has the added advantage of decomposing in two independent stages after application to relatively small particle sizes (between 0.5 and 5μ) so as to assure ready availability of the biocidally active ingredient.

In accordance with one preferred embodiment of the present invention, the ratio by weight of one of the water-soluble polymers to another one of said polymers is from 1:50 to 50:1. Most preferably this ratio ranges from 1:5 to 5:1. Operation with such ratios assures pumpability and fluidity of the aqueous suspensions during the course of preparation, as well as preferred decomposition rates.

As used herein, the term particulate absorbent carrier means all such products commonly used as carriers or diluents in biocidal compositions. Clays such as kaolinite, attapulgite, and montmorillonite, as well as talcum, dolomite, diatomite, gypsum, chalk, ground shale, bentonite, pumice powder, sepiolite and wood powder are typical examples of common absorbent carriers useful for the purpose of the present invention.

By the term "biocidally active ingredient" used herein is meant various herbicides, insecticides, fungicides, etc. Typical examples of these include 2,4 - dichlorophenoxy acetic acid, 2,4 - dichlorophenoxy propionic acid, 2,4 - dichlorophenoxy butyric acid, 2 - methyl - 4 - chlorophenoxy acetic acid, 2 - methyl - 4 - chlorophenoxy propionic acid, 2 - methyl - 4 - chlorophenoxy butyric acid, 2,4,5 - trichlorophenoxy acetic acid, 2,4,5 - trichlorophenoxy propionic acid, beta - naphthoxy acetic acid, salts and esters of the aforesaid acids, 3 - methoxycarbonylamino - phenyl - N - (3' - N - methylphenyl) - carbamate, 3 - *p* - chlorophenyl - 1,1 - dimethyl urea, 6,6 - dichlorobenzonitrile, methylthio - s - triazine; dinitro - o cresol, 2,2 - bis - p - chlorophenyl - 1,1,1 - tri - chloroethane, hexachlorobicyclo - heptene - bis - oxymethylene - sulfide, hexachlorocyclohexane, O,O - dimethyl - 2,2,2 - trichloro - 1 - hydroxyethylphosphate, O,O - dimethyl - S - (2 - oxo - 3 - azobutyl) - dithiophosphate, copper oxychloride, copper - 8 - hydroxyquinoline, zinc ethylenebisdithiocarbamate and manganese ethylenebisdithiocarbamate.

Typical examples of preferred water-soluble polymers include polyvinyl alcohol, polyethylene glycols, polysorbates, calcium and magnesium lignin sulfonates.

It will also be appreciated by those skilled in the art that the aqueous suspensions which are spray-dried may include conventional auxiliary agents such as wetting and dispersing agents, starches, casein, polyphosphates, tannic acid, boric acid and insoluble organic polymers.

By the term "spray drying under mild conditions" used herein is meant spray drying using an ordinary spraying disc at a speed of rotation of about 5,000—7,000 revolutions per minute with an air exhaust temperature of 40—50°C.

The foregoing description of the present invention is for the purpose of illustration and is further illustrated by the following examples; all percentages given being percentages by weight:

Example 1

A mixture of 90 kg. (0,09%) 2 - methyl - 4 - chlorophenoxy acetic acid isooctyl ester, 73 kg. (3,32%) 2,4 - dichlorophenoxy acetic acid isobutyl ester, 50 kg. (2,27%) calcium lignin sulfonate, 20 kg. (0,91%) of polyvinyl alcohol having an average molecular weight of 13,000 500 kg. (22,72%) shale powder of a particle diameter of 2—5μ and 267 kg. (12,14%) attapulgite of a particle diameter of 0.1—3μ is stirred together with 54, 55% water to yield a readily pumpable and sprayable suspension. This suspension is granulated by spray-drying at 6,000 revolutions per minute of the spray disc and an exhaust air temperature of 44—46°C. There are obtained 1,000 kg. of a dry, abrasion-proof granulate having an active ingredient content of 16.3%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0.5—5μ due to the influence of moisture exerted on the plant.

Repetition of the above-described process, but without the use of said polyvinyl alcohol, leads to the formation of a thixotropic, unpumpable and unsprayable paste.

Example 2

A mixture of 160 kg. (16%) 2 - methyl - 4 - chlorophenoxy - propionic acid butyl glycol ester, 41 kg. (4.1%) 2,4 - dichlorophenoxy acetic acid isobutyl ester, 25 kg. (2.5%) calcium lignin sulfonate, 10 kg. (1,0%) of polyvinyl alcohol having an average molecular weight of 13,000, 264 kg. (26.4%) attapulgite of a particle diameter of 0.1—3μ and 500 kg. (50%) water is stirred together and yields a pumpable and sprayable suspension. After spray-drying at 6,000 revolutions per minute of the spray disc and an exhaust air temperature of 42—44°C., there are obtained 500 kg. of a dry, abrasion-proof, granulate having an active ingedient content of 40.2%. The granulate has a grain size of 200—300μ.

On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 3

A mixture of 32 kg. 2,4 - dichlorophen - oxy acetic acid of a particle diameter of 0.1—2μ, 34 kg. 2 - methyl - 4 - chloro - phenoxy acetic acid of a particle diameter of 0.1—2μ and 2.0 kg. of the sodium salt of polymeric, substituted alkyl sulfonic acid is wet-milled with 100 kg. water. The milled material is then mixed with 9 kg. of polyvinyl alcohol having an average molecular weight of 13,000, 15 kg. of polyglycol having an average molecular weight of 200, 208 kg. kaolin of a particle diameter of 1—5μ and 200 kg. water. The pumpable suspension thus obtained has the following composition

5,33% 2,4 - dichlorophenoxy acetic acid
5,66% 2 - methyl - 4 - chlorophenoxy acetic acid
0,33% sodium salt of polymeric, substituted alkyl sulfonic acid
1,5% polyvinyl alcohol
2,5% polyglycol
34,77% kaolin
49,94% water

and is granulated under mild conditions (6,000 revolutions per minute of the spraying disc and an exhaust air temperature of 45—47°C.). There are obtained 300 kg. of a dry, abrasion-proof granulate having an active ingredient content of 22%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 4

A mixture of 7.5 kg. 3 - methoxy - carbonyl - aminophenyl - N - (3' - methyl - phenyl) - carbamate (granulation 15—150μ) and 0.15 kg. sodium isopropylnaphthylsulfate is wet-milled with 8 kg. water to a fineness of 1—3μ. The milled material is subsequently mixed with 0.9 kg. of polyvinyl alcohol having an average molecular weight of 13,000, 1.5 kg. of polyglycol having an average molecular weight of 200, 19.95 kg. kaolin of a particle diameter of 1—5μ and 28.0 kg. water and vigorously stirred. The thus obtained pumpable suspension has the following composition:

11,36% 3 - methoxy - carbonyl - amino - phenyl - N - (3' - methylphenyl) - carbamate
0,23% isopropylnaphthylsulfonate
1,36% polyvinylalcohol
2,34% polyglycol
30,22% kaolin
54,49% water

and is granulated under mild conditions (6,000 revolutions per minute of the spraying disc and an exhaust air temperature of 44—46°C.) to obtain 30 kg. of a dry, abrasion-proof granulate having an active ingredient content of 25%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 5

A mixture of 31 kg. (27,67%) 2,4 - dinitro-o - cresol of a particle diameter of 0.1—3μ, 6.2 kg. (5,54%) calcium lignin sulfonate, 1.25 kg. (1,12%) of polyvinyl alcohol having an average molecular weight of 13,000, 1.85 kg. (1,65%) of "Pluronic L 62" of Wyandotte Chemical Corp. (a copolymer consisting of polyoxyethylene, polyoxypropylene and polyoxyethylene glycol) 15.0 kg. (13,39%) attapulgite of a particle diameter of 0.1—3μ, 6.7 kg. (5,98%) kaolin of a particle diameter of 1—5μ and 50 kg. (44,65%) water is stirred to yield a pumpable and sprayable suspension. After spray-drying under mild conditions (7,000 revolutions per minute of the spraying disc and an exhaust air temperature of 46—48°C.) there are obtained 62 kg. of a dry granulate which has an active ingredient content of 50%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 6

A mixture of 332.5 kg. 2 - methyl - 4 - chlorophenoxy acetic acid, 318.5 kg. 2,4,5 - trichlorophenoxy acetic acid and 60.0 kg. magnesium oxide is wet-milled with 800 kg. water to form the corresponding magnesium salts with a particle diameter of 0.1—3μ. The milled material is subsequently mixed with 500 kg. calcium lignin sulfonate, 100 kg. "Atlox 210" (Atlox 210 is a Trade Mark) of Atlas Goldschmidt GmbH (a mixture of various polyesters on the basis of polysorbate, mono- and diglycerides and propylene glycol), 3722 kg. kaolin of a particle diameter of

1—5μ and 4000 kg. water. After stirring there is obtained a pumpable suspension of the following composition:

3,38% 2 - methyl - 4 - chlorophenoxy acetic acid
3,24% 2,4,5 - trichlorophenoxy acetic acid
0,61% magnesium oxide
5,08% calcium lignin sulfonate
1,02% Atlox 210 (Atlox is a Trade Mark)
37,85% kaolin
48,82% water

which after spray-drying, using a spray disc (6,000 revolutions per minute and an exhaust air temperature of 44—46°C.) yield 5000 kg. of a dry granulate having an active ingredient content of 13,6%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 7

A mixture of 320 kg. (15,24%) 2 - methyl - 4 - chloro - phenoxy propionic acid - n - butyl ester, 90 kg. (4,28%) 2,4,5 - trichloro - phenoxy acetic acid - n - hexyl ester, 20 kg. (0,95%) of polyvinyl alcohol having an average molecular weight of 13,000, 50 kg. (2,38%) calcium lignin sulfonate, 450 kg. (21,43%) attapulgite of a particle diameter of 0.1—3μ, 70 kg. (3,33%) bentonite of a particle diameter of 0.1—2μ and 1100 kg. (52,39%) water is vigorously stirred together. The pumpable suspension thus obtained is spray-dried under mild conditions (6,000 revolutions per minute of the spraying disc and an exhaust air temperature of 43—45°C.). There are obtained 1000 kg. of a granulate having an active ingredient content of 41%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

Example 8

A mixture of 315 kg. (35,0%) manganese ethylenebisdithiocarbamate of a particle diameter of 1—2μ, 35 kg. (3,89%) zinc ethylenebisdithiocarbamate of a particle diameter of 1—2μ, 25 kg. (2,78%) magnesium lignin sulfonate, 15 kg. (1,67%) polyethylene glycol with an average molecular weight of 2,000, 110 kg. (12,27%) kaolin of a particle diameter of 1—5μ and 400 kg. (44,44%) water is vigorously stirred together to form a pumpable suspension. This suspension is subsequently granulated under mild conditions (7,000 revolutions per minute and an exhaust air temperature of 48—50°C.). There are obtained 500 kg. of a granulate having an active ingredient content of 70%. The granulate has a grain size of 200—300μ. On application in the open field, this granulate disintegrates, due to the mechanical effect on the plant, into particles having a size of 50—150μ.

These particles disintegrate on their part into particles of 0,5—5μ due to the influence of moisture exerted on the plant.

WHAT WE CLAIM IS:—

1. A process for the production of a biocidally active granulated composition, comprising forming an aqueous suspension containing 10—50% by weight of a particulate absorbent carrier having a maximum particle diameter of 5μ, 0,5 to 40% by weight of a biocidally active ingredient and from 2 to 10% by weight of water soluble polymers, at least two different polymers being present each of which is a polyalcohol, polyester, polyglycol, polyamide or lignin sulfonate, and spray-drying the suspension under mild conditions, as hereinbefore defined, to produce granules having an average particle size between 200 and 300μ.

2. A process according to claim 1, substantially as hereinbefore described and with reference to any of the specific examples.

3. Biocidally active granulated compositions whenever prepared according to a process as claimed in claims 1 or 2.

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